Макрогетероциклы
http://macroheterocycles.isuct.ru

DOI: 10.6060/mhc140928s

Water–Soluble Pillar[5]arenes: Synthesis and Characterization of the Inclusion Complexes with *p*–Toluenesulfonic Acid

Dmitry N. Shurpik,[a] Luidmila S. Yakimova,[a] Ildar Kh. Rizvanov,[b] Vitaly V. Plemenkov,[c] and Ivan I. Stoikov [a@]

[a]*Kazan Federal University, A.M. Butlerov Chemical Institute, 420008 Kazan, Russian Federation*
[b]*A.E. Arbuzov' Institute of Organic and Physical Chemistry of KSC RAS, 420088 Kazan, Russian Federation*
[c]*Immanuel Kant Baltic Federal University, Institute of Biochemistry, 236041 Kaliningrad, Russian Federation*
[@]*Corresponding author E-mail: ivan.stoikov@mail.ru*

Novel symmetric cationic water-soluble pillar[5]arenes bearing trimethylammonium/methyldiethylammonium groups at both of two rims were synthesized by step-by-step functionalization of the perhydroxylated pillar[5]arene. The recognition ability of water-soluble pillar[5]arenes toward p-toluenesulfoacid was studied. The information on binding mode of the guest inclusion was studied by ^{1}H and 2D NMR spectroscopy. The interaction of synthesized pillar[5]arenes with the substrate and the formation of the 1:1 complexes was shown by UV spectroscopy.

Keywords: Water-soluble pillar[5]arene, synthesis, molecular recognition, heterocycle, macrocycle.

Водорастворимые пиллар[5]арены: синтез и исследование комплексов включения с *п*–толуолсульфокислотой

Д. Н. Шурпик,[a] Л. С. Якимова,[a] И. Х. Ризванов,[b] В. В. Племенков,[c] И. И. Стойков[a@]

[a]*Химический институт им. А.М. Бутлерова, Казанский федеральный университет, 420008 Казань, Россия*
[b]*Институт органической и физической химии им. А.Е. Арбузова Казанского НЦ РАН, 420088 Казань, Россия*
[c]*Балтийский федеральный университет им. И. Канта, Институт биохимии, 236041 Калининград, Россия*

Синтезированы новые катионные водорастворимые пиллар[5]арены, содержащие триметиламмонийные/метилдиэтиламмонийные группы на верхнем и нижнем ободах макроцикла. Исследована их способность к распознаванию п-толуолсульфокислоты.

Ключевые слова: Водорастворимые пиллар[5]арены, синтез, молекулярное распознавание, гетероцикл, макроцикл.

Introduction

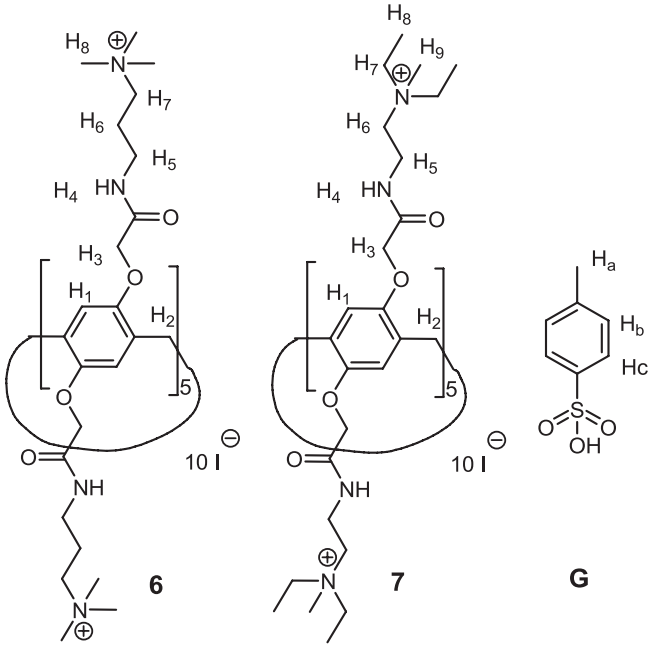
The *p*-cyclophanes attract recently considerable interest of researchers due to the recently disclosed possibility of their synthesis and functionalization of new *p*-cyclophanes, *i.e.* pillar[n]arenes.[1] These unique compounds consist of *p*-hydroquinone fragments coupled by methylene bridges in a macrocycle. Pillar[n]arenes have free hydroxyl groups which can easily be functionalizated.[2,3]

Today, the scope of pillar[n]arenes is very various. These macrocycles are able to selectively bind different kinds of guests and provide useful platform for the construction of various interesting supramolecular systems. In literature, complexation properties of pillar[n]arenes with various types of molecules in the organic media were noted.[4] However, the greatest interest is in using water as a solvent.[5] The solvent properties of water are vital in biology because many biochemical reactions take place only

in aqueous solutions. In addition, water is used to transport of biological molecules.

Based on mentioned above, the mail goal of this work involves synthesis of water-soluble pillar[n]arenes and study of their inclusion complexes.

We have obtained water-soluble pillar[n]arenes containing carbonyl and ammonium groups. *p*-Toluenesulfoacid (**G**) was chosen as a substrate because it contains aromatic ring which can be involved in electron rich macrocycle cavity and because it is well dissolved in water to carry out reactions in homogeneous conditions.



Experimental

General

^{1}H NMR spectra were recorded on the Bruker Avance-400 (400 MHz) spectrometer and ^{13}C and 2D NOESY NMR spectra were obtained on the impulse spectrometer Bruker Avance II (with 125 MHz and 500 MHz respectively). Chemical shifts were determined against the signals of residual protons of deuterated solvents ($CDCl_3$, CD_3COCD_3, CD_3SOCD_3, D_2O). The concentration of sample solutions was 3-5%.

Attenuated total internal reflectance IR spectra were recorded with Spectrum 400 (Perkin Elmer) Fourier spectrometer.

Elemental analysis was performed with Perkin Elmer 2400 Series II instrument.

The mass spectra were obtained on Bruker Ultraflex III MALDI-TOF instrument using 4-nitroaniline matrix.

Melting points were determined using the Boetius Block apparatus.

Additional control of the purity of compounds and monitoring of the reaction were carried out by thin-layer chromatography using Silica G, 200 μm plates, UV 254.

Most chemicals were purchased from Aldrich and used as received without additional purification. Organic solvents were purified in accordance with standard procedures.

Determination of stability constant and stoichiometry of the complex by the UV titration. The UV measurements were performed with "Shimadzu UV-3600" instrument. The $0.8\cdot10^{-3}$ M solution of *p*-toluenesulfoacid (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 μl) in water was added to 0.5 ml of the solution of receptors **6** and **7** ($3\cdot10^{-4}$ M) in water and diluted to final volume of 3 ml with water. The UV spectra of the solutions were then recorded. The stability constant and stoichiometry of complexes were calculated as described elsewhere.[8] Three independent experiments were carried out for each series. Student's t-test was applied in statistical data processing.

Synthesis

*General procedure of the synthesis of the compounds **1-3.*** Initial 1,4-dimethoxypillar[5]arene **1** was obtained from commercially available 1,4-dimethoxybenzene by literary method.[6] Further removal of methoxyl protections led to pillar[5]arene **2**.[7] Pillar[5]arene with ethoxycarbonyl fragments **3** was obtained by the reaction of compound **2** with ethyl bromoacetate.

*1,4-Dimethoxypillar[5]arene (**1**).* Product yield: 80 %. Mp: 249 °C, 248.8 °C.[6] ^{1}H NMR ($CDCl_3$) δ_H ppm: 3.74 (s, 30H, $-OCH_3$), 3.76 (s, 10H, $-CH_2-$), 6.80 (s, 10H, ArH). MALDI-TOF MS $C_{45}H_{50}O_{10}$: calculated $[M^+]$ *m/z*=750.3, found $[M+Na]^+$ *m/z*=773.4, $[M+K]^+$ *m/z*=789.5.

*Pillar[5]arene (**2**).* Product yield: 91 %. The decomposition was observed at 230 °C without melting. ^{1}H NMR (CD_3COCD_3) δ_H ppm: 3.66 (s, 10H, $-CH_2-$), 6.64 (s, 10H, ArH), 7.99 (s, 10H, -OH). MALDI-TOF MS $C_{35}H_{30}O_{10}$: calculated $[M^+]$ *m/z*=610.2, found $[M+Na]^+$ *m/z*=633.1, $[M+K]^+$ *m/z*=649.2.

*4,8,14,18,23,26,28,31,32,35-Deca-[(ethoxycarbonyl)-methoxy]pillar[5]arene (**3**).* Product yield: 80 %. Mp: 199 °C, 196.7 °C.[6] ^{1}H NMR ($CDCl_3$) δ_H ppm: 0.96 (m, 30H, $-CH_2CH_3$), 3.86 (s, 10H, $-CH_2-$), 4.09 (m, 20H, $-CH_2CH_3$), 4.55 (dd, 20H, $O-CH_2C(O)-$), 7.04 (s, 10H, ArH). MALDI-TOF MS: calculated $[M^+]$ *m/z*=1471.24, found $[M+Na]^+$ *m/z*=1494.28.

*General procedure of the synthesis of the compounds **4** and **5**.* In a round-bottom flask equipped with magnetic stirrer, the compound **3** (0.30 g, 0.2 mmol), 10 ml methanol and *N,N*-diethylethane-1,2-diamine (0.35 g, 3.1 mmol, 0.43 ml) or *N,N*-dimethylpropane-1,3-diamine (0.31 g, 3.1 mmol, 0.38 ml) were refluxed for 72 hrs. The residue was dissolved in a minimum amount of chloroform and washed several times with distilled water. The organic layer was separated and dried (mol. sieves, 3 Å), the solvent was removed under reduced pressure. The residue was dried under reduced pressure during 30 min. Light-yellow viscous oil was received.

*4,8,14,18,23,26,28,31,32,35-Decakis-[(N-(3',3'-dimethyl aminopropyl)carbamoylmethoxy]pillar[5]arene (**4**).* Product yield: 0.30 g (72 %). ^{1}H NMR (CD_3SOCD_3) δ_H ppm: 1.27 (m, 20H, $=NCH_2CH_2CH_2NH-$), 1.95 (m, 20H, $=NCH_2CH_2CH_2NH-$), 2.01 (s, 60H, $(CH_3)_2N-$), 3.01 (m, 20H, $=NCH_2CH_2CH_2NH-$), 3.8 (s, 10H, $-CH_2-$), 4.37 (dd, 20H, $O-CH_2C(O)-$), 6.83 (s,10H, ArH), 7.74 (t, 10H, $^3J_{HH}$=5.1 Hz, -C(O)NH). ^{13}C NMR (CD_3SOCD_3) δ_C ppm: 167.77, 148.79, 127.58, 114.44, 67.19, 56.57, 45.14, 37.10, 28.79, 26.47. ^{1}H-^{1}H NOESY (NOE) (the major cross-peaks): H^4/H^6; H^4/H^5; H^1/H^2; H^3/H^1; H^2/H^3; H^8/H^3; H^1/H^4; H^3/H^4; H^6/H^7. IR ν cm^{-1}: 3288.59, 3079.05 (N-H), 1655.47 (C=O). MALDI-TOF MS: calculated $[M^+]$ *m/z*=2032.3, found $[M+H]^+$ *m/z*=2033.3, $[M+Na]^+$ *m/z*=2055.3. Found: C, 62.04; H, 8.43; N, 13.78. $C_{105}H_{170}N_{20}O_{20}$. Calculated for $C_{105}H_{170}N_{20}O_{20}$: C, 61.05; H, 8.65; N, 12.68.

*4,8,14,18,23,26,28,31,32,35-Decakis-[(N-(2',2'-diethyl-aminoethyl)carbamoylmethoxy]pillar[5]arene(**5**).* Product yield: 0.52 g (71 %). ^{1}H NMR (CD_3SOCD_3) δ_H ppm: 0.91 (t, 60H, $^3J_{HH}$=7.1 Hz, $-N(CH_2CH_3)_2$), 2.41-2.52 (m, 60H, $-CH_2CH_2-N(CH_2CH_3)_2$), 3.24 (m, 20H, $-CH_2CH_2-N(CH_2CH_3)_2$), 3.79 (s, 10H, $-CH_2-$), 4.32 (s, 20H, $O-CH_2C(O)-$), 6.85 (s,10H, ArH), 7.86 (t, 10H, $^3J_{HH}$=5.2 Hz, -C(O)NH). ^{13}C NMR (CD_3SOCD_3) δ_C ppm: 167.64, 148.95, 127.97, 114.71, 67.71, 51.37, 46.47, 36.59, 28.80, 11.75. ^{1}H-^{1}H NOESY (NOE) (the major cross-peaks): H^8/H^4; H^7/H^4; H^5/H^4; H^2/H^4; H^3/H^4; H^1/H^4; H^1/H^8; H^1/H^7; H^1/H^5; H^1/H^5; H^1/H^2; H^1/H^3; H^3/H^8; H^3/H^7; H^3/H^5; H^3/H^1; H^2/H^8; H^2/H^7; H^2/H^5; H^2/H^3; H^5/H^6; H^8/H^7. IR ν cm^{-1}:

3311.05 (N-H), 1661.33 (C=O). MALDI-TOF MS: calculated $[M^+]$ *m/z*=2172.4, found $[M+H]^+$ *m/z*=2173.4, $[M+Na]^+$ *m/z*=2195.4. Found: C, 63.57; H, 8.81; N, 12.89. $C_{115}H_{190}N_{20}O_{20}$. Calculated for $C_{115}H_{190}N_{20}O_{20}$: C, 63.02; H, 8.55; N, 12.49.

*General procedure of the synthesis of the compounds **6** and **7**.* Equimolar amount of methyl iodide was added to the solution of the compound **4** (0.30 g, 0.15 mmol) or **5** (0.30 g, 0.14 mmol) in 10 ml acetonitrile. Reaction mixture was refluxed for 72 hrs and the solvent was removed under reduced pressure. The powder obtained was dried under reduced pressure (P_2O_5).

*4,8,14,18,23,26,28,31,32,35-Decakis-[(N-(3',3',3'-trimethylammoniumpropyl)carbamoylmethoxy]pillar[5]arene decaiodide (**6**).* Product yield: 0.48 g (96 %). Mp: 124 °C. ^{1}H NMR (CD_3SOCD_3) δ_H ppm: 1.93 (m, 20H, =NCH$_2$C*H*$_2$CH$_2$NH-), 3.13 (s, 90H, $(CH_3)_3N^+$-), 3.25 (m, 20H, =NCH$_2$CH$_2$C*H*$_2$NH-), 3.39 (m, 20H, =NC*H*$_2$CH$_2$CH$_2$NH-), 3.9 (s, 10H, -CH$_2$-), 4.41 (dd, 20H, O-CH$_2$C(O)-), 6.83 (s, 10H, ArH), 7.74 (t, 10H, $^3J_{HH}$=5.6 Hz, -C(O)NH). ^{13}C NMR (CD_3SOCD_3) δ_C ppm: 170.89, 149.48, 129.88, 116.22, 68.30, 64.09, 53.09, 35.88, 29.12, 22.68. ^{1}H-^{1}H NOESY (NOE) (the major cross-peaks): H^1/H^3; H^2/H^1; H^4/H^8; H^5/H^6; H^7/H^8; H^3/H^2. IR ν cm^{-1}: 3285.31, 3386.07 (N-H), 1662.39 (C=O). MALDI-TOF MS: calculated $[M–I^-]^+$ *m/z*=3324.6, found $[M–I^-]^+$ *m/z*=3325.2. Found: C, 40.01; H, 5.84; N, 8.13. $C_{115}H_{200}N_{20}O_{20}$. Calculated for $C_{115}H_{200}N_{20}O_{20}$: C, 39.05; H, 5.43; N, 8.10.

*4,8,14,18,23,26,28,31,32,35-Decakis-[(N-(2'-methyl-2',2'-diethylaminoethyl)carbamoylmethoxy]pillar[5]arene (**7**).* Product yield: 0.45 g (88 %). Mp: 153 °C. ^{1}H NMR (CD_3SOCD_3) δ_H ppm: 1.32 (t, 60H, $^3J_{HH}$=6.1 Hz, -N(CH$_2$C*H*$_3$)$_2$), 3.02 (s, 30H, -N-CH$_3$), 3.41 (m, 40H, -CH$_2$C*H*$_2$-N(C*H*$_2$CH$_3$)$_2$), 3.77 (m, 20H, -C*H*$_2$CH$_2$-N(CH$_2$CH$_3$)$_2$), 4.01 (s, 10H, -CH$_2$-), 4.20 (d, 10H, AB-system, $^2J_{HH}$=15.1 Hz, O-C*H*$_2$C(O)NH-), 4.40 (d, 10H, AB-system, $^2J_{HH}$=15.1 Hz, O-C*H*$_2$C(O)NH-), 6.76 (s, 10H, ArH). ^{13}C NMR (CD_3SOCD_3) δ_C ppm: 171.06, 149.17, 128.90, 115.35, 67.88, 64.09, 57.74, 57.17, 47.48, 32.68, 30.36, 7,50. ^{1}H-^{1}H NOESY (NOE) (the major cross-peaks): H^1/H^8; H^7/H^1; H^3/H^8; H^6/H^7; H^8/H^9. IR ν cm^{-1}: 1665.92 (C=O), 3331.48 (N-H), 1665.92 (C=O). MALDI-TOF MS: calculated $[M–I^-]^+$ *m/z*=3591.73, found $[M–I^-]^+$ *m/z*=3463.7. Found: C, 41.79; H, 6.17; N, 7.80. $C_{125}H_{220}N_{20}O_{20}$. Calculated for $C_{125}H_{220}N_{20}O_{20}$: C, 40.53; H, 5.93; N, 7.45.

Results and Discussion

*Synthesis of Pillar[5]arenes **6** and **7***

As the molecular recognition in water is of special interest due to mimicking recognition events in biological systems, much attention has been devoted to the development of water soluble pillar[n]arenes as hosts with high binding selectivity in biological applications. In this context, we have synthesized two novel water-soluble pillar[5]arene derivatives with varied length of the spacer between amide and ammonium groups (ethylene, propylene) and the substituent (ethyl, methyl) at ammonium fragment.

According to the goal, novel approach to the synthesis of the water-soluble pillar[5]arenes has been developed. Contrary to first precursors of water-soluble pillar[5]arenes containing either carbonyl or ammonium groups, we proposed a combination of these structural fragments by aminolysis of the ester groups. Several steps were involved in the method.

Pillar[5]arene with ethoxycarbonyl fragments **3** was used as precursor in the synthesis of water-soluble pillar[5]arene due to simplicity of its aminolysis. According to literary, decamethoxypillar[5]arene **1** was first synthesized from commercially available reagents. Then, it was hydrolyzed to perhydroxylated pillar[5]arene **2** which was involved in the reaction with ethyl ester of bromoacetic acid in the presence of potassium carbonate in acetonitrile (Scheme 1). The base and solvent were specified in accordance with their efficiency in alkylation of *p-tert*-butyl thiacalix[4]arene at the lower rim.[9,10] Besides, KI as catalyst was used in alkylation to increase the product yield.[11]

To prepare compounds **4** and **5** with high yields, the process included the reaction of the macrocycle **3** with *N*,*N*-diethylethane-1,2-diamine and *N*,*N*-dimethylpropane-1,3-diamine in methanol. This approach was successfully applied to the synthesis of *p-tert*-butyl thiacalix[4]arene derivatives and made it possible to obtain functionalized macrocycles with high yields.[10,12-14]

The introduction of suitable substituents at both upper and lower rims of the macrocycle **4**, **5** was supposed to give water soluble compounds **6** and **7**. For this purpose, the compounds **4** and **5** were treated with methyl iodide in acetonitrile. The compounds **6** and **7** containing ten ammonium groups at upper and lower rims were obtained as white solids (96 and 88 % yields, respectively). The solvent was chosen in accordance with their efficiency in Mishutkin´s alkylation.[15] Pillar[5]arenes **6** and **7** can be easily dissolved in water to give colorless solution. Furthermore, the compounds **6** and **7** synthesized were found to be hygroscopic. They become soft in moist environment in a short time, though remain solid in dry environment.

Thus, interaction of the macrocycle **4** and **5** with methyl iodide made it possible to obtain water-soluble pillar[5]arenes **6** and **7** containing both carbonyl and ammonium fragments in the structure (Scheme 1). Because of large number of the reactive centers, the reaction was carried out within 72 hours.

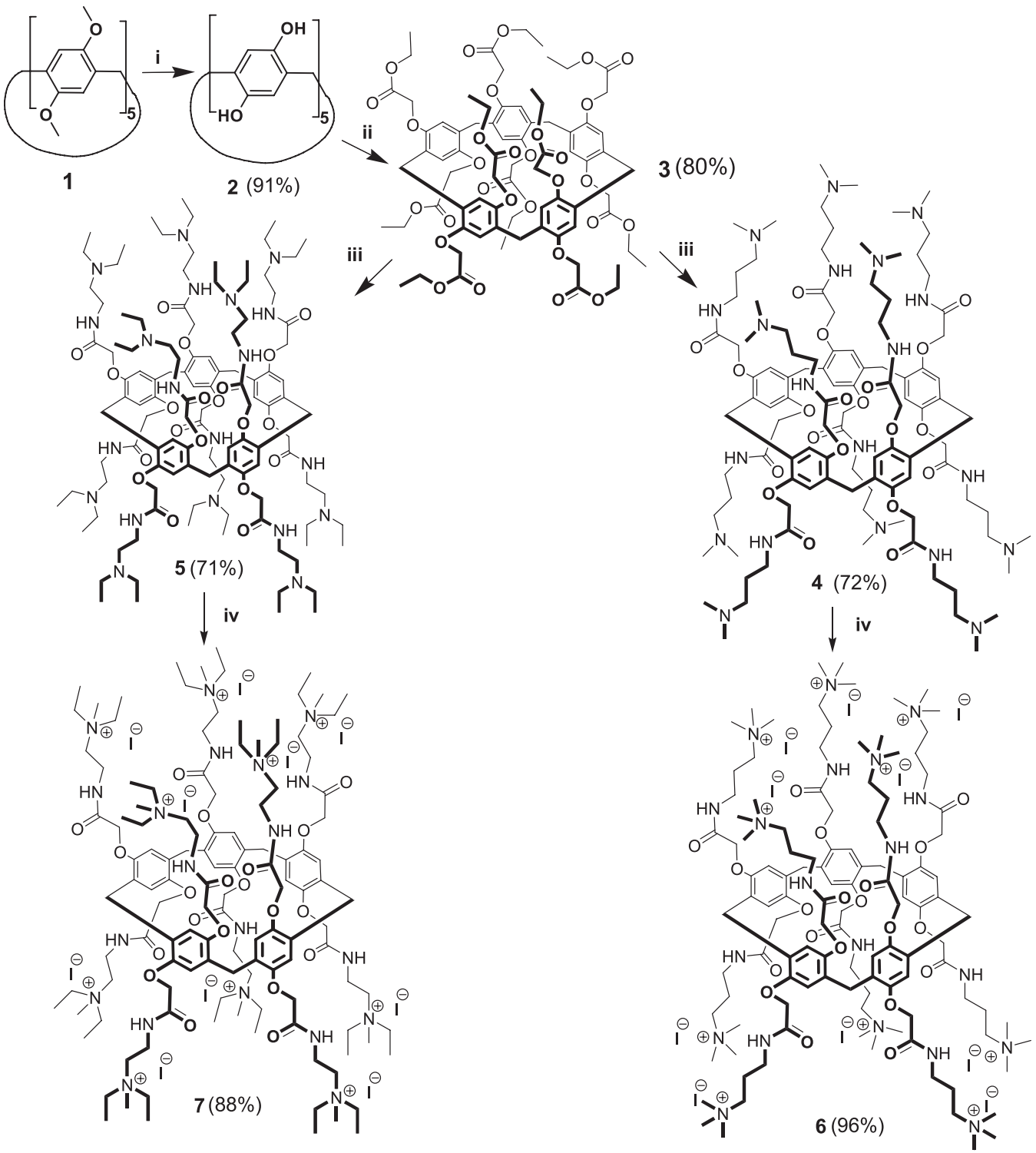
New compounds **4**-**7** were fully characterized by NMR ^{1}H, ^{13}C, 2D NMR NOESY ^{1}H-^{1}H, IR spectroscopy, mass spectrometry (MALDI-TOF) and elemental analysis.

Figure 1 shows the ^{1}H NMR spectrum of the compound **5** in which proton signals of aromatic, oxymethylene groups and methylene bridge in macrocycle appear as singlets at 6.85, 4.32 and 3.79 ppm, respectively. The methylene protons between amide and amine groups were observed as multiplets at 3.24–2.41 ppm. The methyl groups appear as triplet at 0.91 ppm ($^3J_{HH}$=7.1 Hz). The triplet of amide protons (7.86 ppm, $^3J_{HH}$=5.2 Hz) indicates fully aminolyzed product.

The chemical shifts, integrated intensity and multiplicity of the all proton signals in the ^{1}H NMR for compound **5** are in good agreement with those proposed for such structure.

As an example, the MALDI-TOF mass spectrum of the pillar[5]arene **4** (M($C_{105}H_{170}N_{20}O_{20}$)=2032.3) is shown in Figure 2. In the MALDI-TOF mass spectrum of the compound **4** the peaks of the molecular ion (*m/z* (M^+)=2033.3), molecular ion with sodium cation (*m/z* ($M+Na^+$)=2055.3) are presented.

Thus, new water-soluble pillar[5]arenes were synthesized. The structure of the compounds obtained was characterized by ^{1}H NMR, ^{13}C, IR spectroscopy and mass spectrometry (MALDI-TOF). The spatial structure of new functionalized pillar[5]arenes was established by two-dimensional 2D NMR NOESY ^{1}H-^{1}H spectroscopy.



Scheme 1. Reagents and conditions: i - $CHCl_3$, BBr_3; ii – ethyl bromoacetate/K_2CO_3, KI, acetonitrile, reflux; iii - MeOH, *N,N*-dimethylpropane-1,3-diamine or *N,N*-diethylethane-1,2-diamine, reflux; iv – MeI, CH_3CN, reflux.

*Complexation Study of Pillar[5]arenes **6** and **7** by NMR and UV Spectroscopies*

Pillar[n]arenes are able to recognize guest molecules in different solvents by inclusion complex formation mostly due to lipophilic molecular cavity, CH-π interactions and solvophobic effects. Because of ten positive charges present at the macrocycle ring, the compound **6** and **7** can play the role of anion receptor. In this work, we studied the recognition of *p*-toluenesulfoacid as a guest by water-soluble pillar[5]arenes **6** and **7** with I^- as counter ion as hosts. The choice of the guest is caused by its ability to form inclusion complexes with aromatic hosts and also by the ability of *p*-toluenesulfoacid to be dissolved in water.

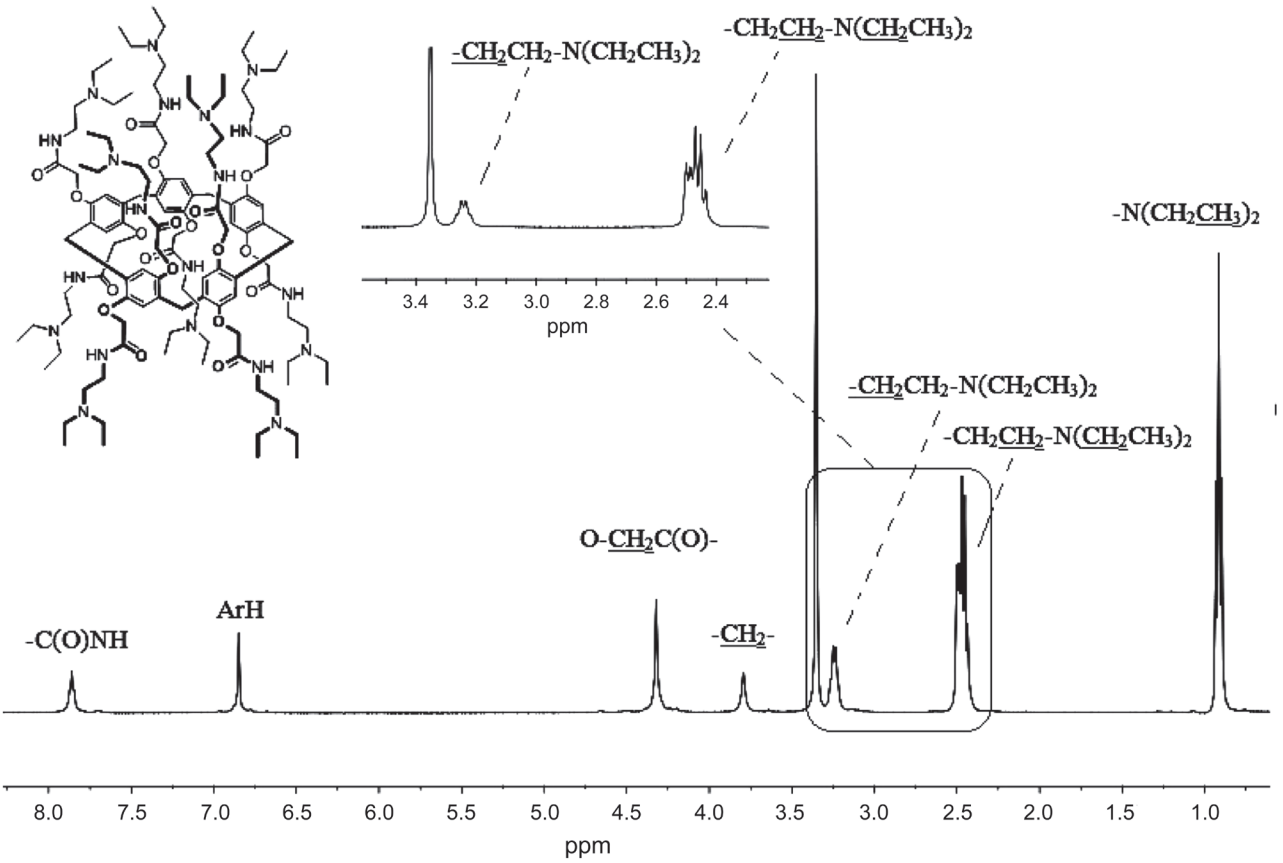


Figure 1. ^{1}H NMR spectrum of compound **5** (CD_3SOCD_3, at 25 °C, Bruker Avance-400).

The ^{1}H NMR spectroscopy allows getting detailed information on the structure and composition of pillar[5] arenes and their complexes in solution. To obtain information on the binding mode of the inclusion of guest (**G**) in host (**H**), ^{1}H and 2D NMR experiments were performed. Figure 3 shows the ^{1}H NMR spectra of **G** in D_2O recorded in the absence and presence of one equivalent of **H**. We compared the ^{1}H NMR spectra of initial water-soluble pillar[5]arene **7** (**H**), *p*-toluenesulfoacid (**G**) and their complex.

The strong upfield shift of the aromatic and methyl signals testifies the complex formation. It should be noted, that δ ($\mathbf{H_a}$) > δ ($\mathbf{H_b}$) > δ ($\mathbf{H_c}$). Thus, methyl group of **G** should be deeper incorporated into the macrocycle cavity of **H**. Also, the host proton signals $\mathbf{H_3}$ appeared as two duplets, but in complex they integrate into one singlet. This integrating is possibly due to influence of magnetic field of phenyl fragment in the guest molecule.

To confirm this information, 2D NMR NOESY ^{1}H-^{1}H for this complex was obtained (Figure 4). As can be seen, aromatic protons of **G** ($\mathbf{H_c}$) exhibit cross-peaks with $\mathbf{H_7}$ and $\mathbf{H_3}$ of the host. The methyl protons of *p*-toluenesulfoacid ($\mathbf{H_a}$) show cross-peaks with protons of methylene bridge ($\mathbf{H_2}$) and methoxycarbonyl fragment ($\mathbf{H_3}$). Thus, we can conclude that guest is included into cavity of pillar[n]arene and the inclusion complex is formed.

For quantifying host-guest interactions, the UV-titration of the host by the guest solution is most popular. Changes in the absorbance spectrum of the pillar[5]arenes **6** and **7** after addition of *p*-toluenesulfoacid indicated the formation of their complexes with the substrates. The interaction between guest and pillar[5]arenes in water monitored by UV-spectroscopy showed changes in the absorbance spectrum of the macrocycles at 260-320 nm (Figure 5). To quantify molecular recognition of the *p*-toluenesulfoacid by pillar[5] arenes **6**, **7**, the stability constants and the stoichiometry of the macrocycle-substrate complex formed in the water were established.

It was shown that the interaction of pillar[5]arenes **6**, **7** with the substrate led to formation of 1:1 complexes. The calibration curve shows good linearity with the correlation coefficient of 0.9951. Thus, pillar[5]arenes **6** and **7** form inclusion complexes with *p*-toluenesulfoacid. Earlier it was shown catalytic amounts of *p*-toluenesulfonic acid led to oligomerization of monomers (2,5-bis(benzyloxymethyl)-1,4-diethoxybenzene) delivering the cyclic pentamer **1**.[16] Therefore we can propose *p*-toluenesulfonic acid is the template in synthesis pillar[5]arenes.

The logK_{ass} values of the complexes **6** and **7** with *p*-toluenesulfoacid are 1.43±0.12 and 1.22±0.08 correspondingly. The K_{ass} values are lower by one order of K_{ass} value of the previously reported complex of water-soluble pillar[5]arene.[17]

Conclusion

In summary, we have successfully synthesized symmetric cationic water-soluble pillar[5]arene bearing

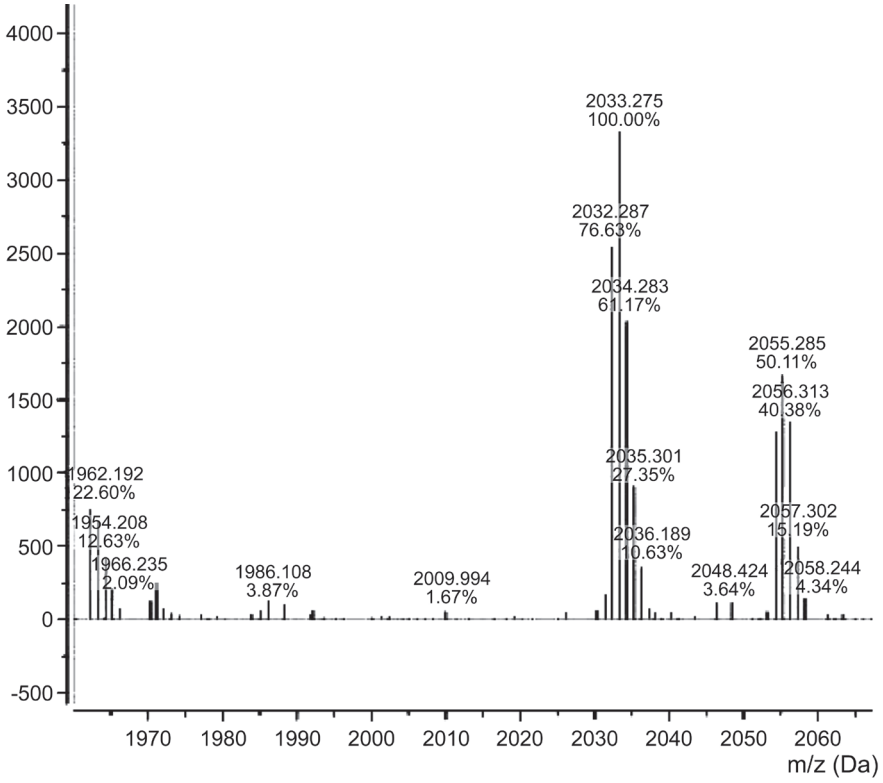


Figure 2. MALDI-TOF mass spectrum of compound **4**.

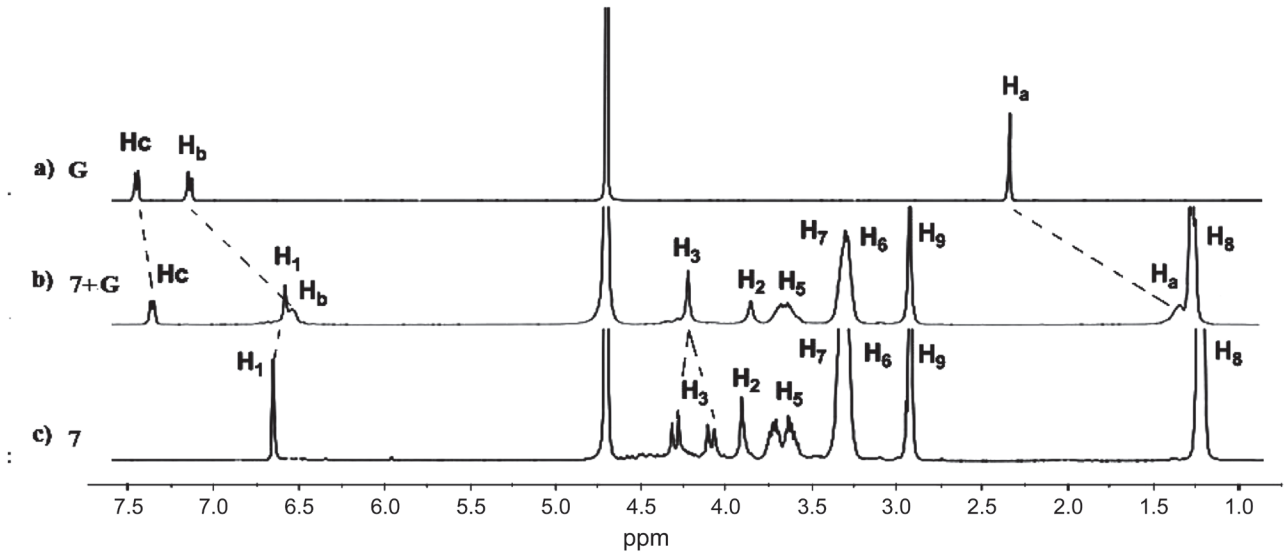


Figure 3. ^{1}H NMR spectra (D_2O, 293 K, 400 MHz): a) *p*-toluenesulfoacid (**G**) (0.0112 mol/l); b) *p*-toluenesulfoacid (**G**) (0.0112 mol/l) + **7** (0.0112 mol/l); c) **7** (0.0112 mol/l).

trimethylammonium/methyldiethylammonium groups at both of rims. The presence of ten positive charges makes it possible to act as an anion receptor. The recognition ability of *p*-toluenesulfoacid (**G**) by water-soluble pillar[5]arenes (**H**) with I^- as counter ion was studied. By ^{1}H and 2D NMR experiments, the information on binding mode of the inclusion of **G** in **H** was obtained. Thus, the methyl group of **G** should be more incorporated into the macrocycle cavity of **H**. Using UV spectroscopy, it was shown that the interaction of pillar[5] arenes **6**, **7** with the substrate led to formation of 1:1 complexes with $\log K_{ass}$ of about 1.43 and 1.22 respectively.

Acknowledgements. The work was supported by Russian Scientific Foundation (№ 14-13-00058).

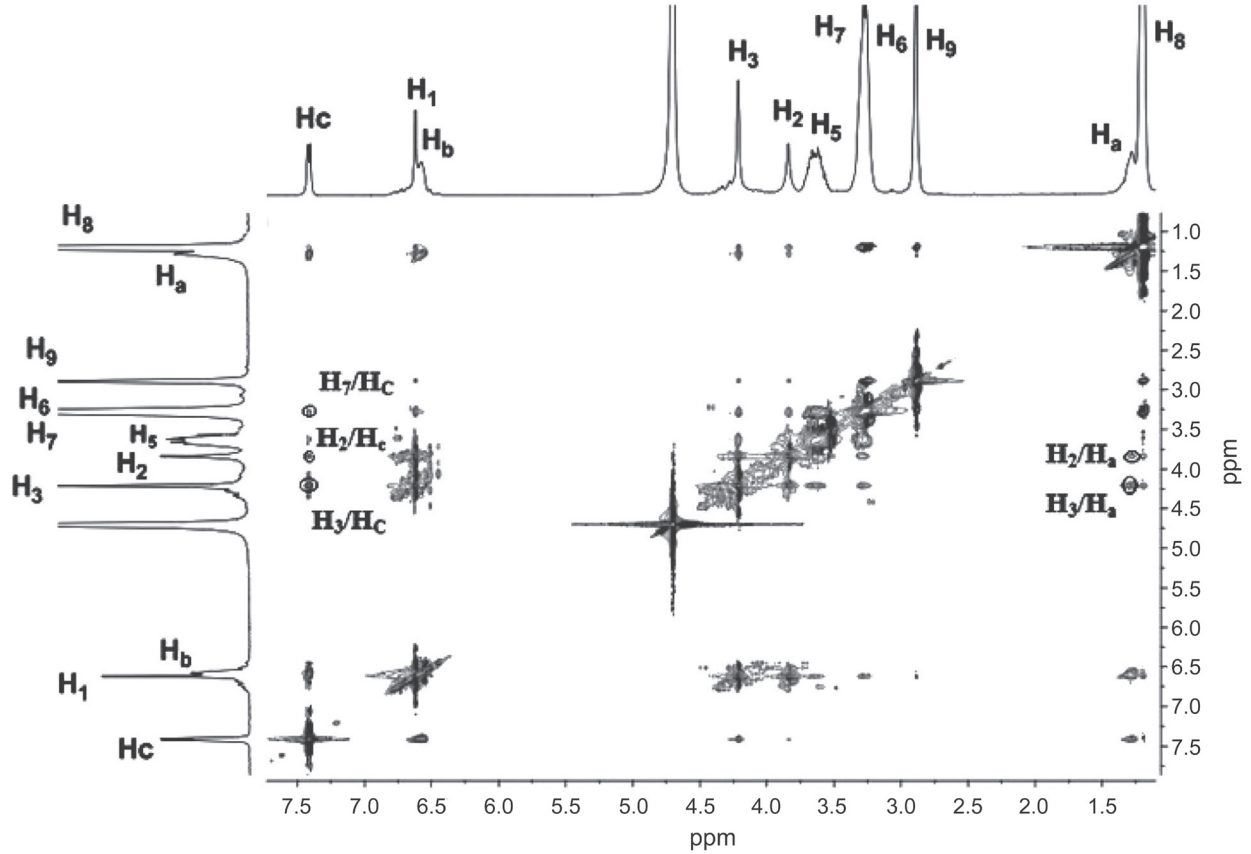


Figure 4. 2D NMR NOESY ^{1}H-^{1}H spectrum for mixture of **7** (0.0112 mol/l) and **G** (0.0112 mol/l) in D_2O at 293 K.

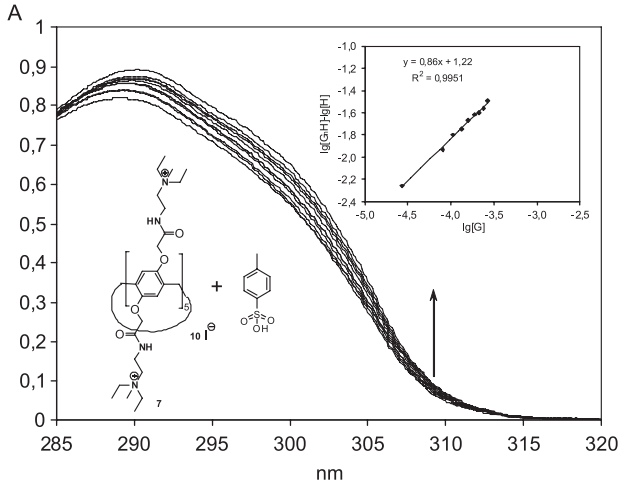


Figure. 5. Spectrophotometric titration of system pillar[5]arene **7** and *p*-toluenesulfoacid in water. The insets show the titration curve.

References

1. Strutt N.L., Zhang H., Schneebeli S.T., Stoddart J.F. *Acc. Chem. Res*. **2014**, *47*, 2631−2642.
2. Cao D., Meier H. *Asian J. Org. Chem.* **2014**, *3*, 244–262.
3. Ogoshi T., Kanai S., Fujinami Sh., Yamagishi T., Nakamoto Y. *J. Am. Chem. Soc.* **2008**, *130*, 5022–5023.
4. Ogoshi T. *Chem. Commun*. **2014**, *50*, 4776-–4787.
5. Ma Y., Ji X., Xiang F., Chi X., Han C., He J., Abliz Z., Chena W., Huang F. *Chem. Commun.* **2011**, *47*, 12340–12342.
6. Boinski T., Szumna A. *Tetrahedron* **2012**, *68*, 9419-9422.
7. Ogoshi T., Aoki T., Kitajima K., Fujinami S., Yamagishi T., Nakamoto Y. *J. Org. Chem.* **2011**, *76*, 328–331.
8. Yushkova E.A., Stoikov I.I., Zhukov A.Yu., Puplampu J.B., Rizvanov I.K., Antipin I.S., Konovalov A.I. *RSC Adv.* **2012**, *2*, 3906–3919.
9. Vavilova A.A., Nosov R.V., Yakimova L.S., Antipin I.S., Stoikov I.I. *Macroheterocycles* **2013**, *6*, 219–226.
10. Stoikov I.I., Vavilova A.A., Badaeva R.D., Gorbachuk V.V., Evtugyn V.G., Sitdikov R.R., Yakimova L.S., Zharov I. *J. Nanopart. Res.* **2013**, *15*, 1617–1631.
11. Stoikov I.I., Gafiullina L.I., Ibragimova D.S., Antipin I.S., Konovalov A.I. *Russ. Chem. Bull., Int. Ed.* **2004**, *53*, 1172–1180.
12. Galukhin A.V., Zaikov E.N., Antipin I.S., Konovalov A.I., Stoikov I.I. *Macroheterocycles* **2012**, *5*, 266–274.
13. Galukhin A.V., Shabalin K.V., Antipin I.S., Konovalov A.I., Stoikov I.I. *Mendeleev Commun.* **2013**, *23*, 41–43.
14. Galukhin A.V., Andreyko E.A., Rizvanov I.H., Stoikov I.I. *Mendeleev Commun*. **2013**, *23*, 196–198.
15. Smith M.B., March J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure.* Hoboken: John Wiley & Sons, Inc, **2007**. 2357 p.
16. Cao D., Kou Y., Liang J., Chen Z., Wang L., Meier H. *Angew. Chem., Int. Ed*. **2009**, *48*, 9721–9723.
17. Ogoshi T., Hashizume M., Yamagishi T., Nakamoto Y. *Chem. Commun.* **2010**, *46*, 3708–3710.

Received 14.09.2014
Accepted 11.12.2014